N74-33865

Unclas 33/13 49631

CHLORIDE IN THE THE THE DUAL ISOTOPE BECKELEY, CALIF.)

(NASA-CR-132520) THE CONTINUOUS MEASUREMENT OF HYDROGEN CHLORIDE AMBIENT ATMOSPHERE USING THE DUAL INFRARED (Andros, Inc., Berkeley, 31 p HC 83 25



THE CONTINUOUS MEASUREMENT OF HYDROGEN CHLORIDE IN THE AMBIENT ATMOSPHERE USING THE DUAL ISOTOPE INFRARED ABSORPTION TECHNIQUE

By Kevin G. Williams February 1974 ARFR-66



Prepared under Contract No. NAS1-12404 by
ANDROS INCORPORATED
2332 Fourth Street
Berkeley, California 94710
for
LANGLEY RESEARCH CENTER
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

THE CONTINUOUS MEASUREMENT OF HYDROGEN CHLORIDE IN THE AMBIENT ATMOSPHERE USING THE DUAL ISOTOPE INFRARED ABSORPTION TECHNIQUE

By Kevin G. Williams
February 1974

ARFR-66

Prepared under Contract No. NAS1-124-4 by

ANDROS INCORPORATED

2332 Fourth Street
Berkeley, California 94710

for

LANGLEY RESEARCH CENTER
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

# ANDROS INCORPORATED

# TABLE OF CONTENTS

| Section | <u>Title</u>   | Page |
|---------|--|------|
| ,1      | INTRODUCTION   | 1-1  |
| 2       | PRINCIPLE OF THE DUAL ISOTOPE GAS FILTER CORRELATION NDIR GAS ANALYZER | 2-1  |
| 3       | DESCRIPTION OF THE PROTOTYPE HCl ANALYZER                              | 3-1  |
| 4       | RESULTS OBTAINED WITH THE PROTOTYPE HC1 ANALYZER                       | 4-1  |
|         | 4.1 Test Apparatus   | 4-1  |
|         | 4.2 Sensitivity  | 4-3  |
| •       | 4.3 Response Time  | 4-5  |
| •       | 4.4 Specificity  | 4-5  |
| •       | 4.5 Stability  | 4-5  |
|         | 4.6 Effect of H <sub>2</sub> O Vapor on Span Sensitivity               | 4-10 |
| 5       | CONCLUSIONS AND RECOMMENDATIONS  | 5-1  |

#### 1. INTRODUCTION

The gaseous species hydrogen chloride is an important combustion by-product of certain propellants commonly used in rocket propulsion. Since there are probably no naturally occurring sources of this gas, little is known about its dispersal patterns and the reactive processes it can undergo in the ambient atmosphere. With the proposed increasing use of rocket-propelled space vehicles, it becomes important that the toxic combustion effluents and their dispersal patterns be characterized. A trace gas analyzer capable of measuring hydrogen chloride to the required degree of sensitivity will be one of the important tools in such investigations.

This report contains the results of a program to develop a prototype gas filter correlation NDIR analyzer capable of providing the required HCl measurement capability, while maintaining an adequate rejection of any other gases anticipated in the atmosphere. Examples of the performance of the prototype analyzer are presented which show an rms noise equivalent concentration of 0.06 ppm of HCl has been achieved while maintaining an electronically determined 10-90% time response to gas samples of about 2 seconds. no measureable response has been observed to CO2, CO and H2O while maintaining an adequate rejection of the hydrocarbons, for example CH, and n-hexane. Furthermore, experiments have been performed which have both demonstrated that the span stability of the HCl gas filter correlation analyzer is unaffected by the presence of water vapor; and, in addition, support the belief that the incorporation of a relatively open-volume, multiple path sample cell into the instrument would enable ground station as well as airborne measurements of trace quantities of HCl in the ambient atmosphere to be performed.

This report first gives a brief account of the principle of the gas filter correlation technique as applied to HCl in Section 2, which is followed by a description of the prototype analyzer in Section 3. Section 4 describes the conditions under which test results were obtained, as well as presenting graphical results of the sensitivity, response time, stability, specificity and detection of HCl in the presence of moisture. Finally, the general conclusions and recommendations are given in Section 5.

# 2. PRINCIPLE OF THE DUAL ISOTOPE GAS FILTER CORRELATION NDIR GAS ANALYZER

The Gas Filter Correlation technique belongs to the nondispersive infrared class of analyzers. In the present application, two cells containing two stable isotopic species of hydrogen chloride, namely H<sup>35</sup>Cl and H<sup>37</sup>Cl respectively, are mounted in a chopper assembly and rotated at high speed so as to alternately filter radiation emitted from an infrared source. The intensity of the radiation transmitted through the gas sample and an interference filter overlapping the strong 3.5um band of HCl is determined using a temperature stabilized PbSe detector. concentration of HCl present in the sample gas is determined by normalizing the change it produces in the difference between the two filter cell signals to that of their average signal. the instrument span is rendered insensitive to changes in the source emission and optical transmission. A schematic diagram illustrating the principle of the Gas Filter Correlation Analyzer is shown in Figure 2.1.

The filtered and chopped infrared beam presents in time sequence to the solid state detector, two similar but importantly differing spectra. One spectrum is missing those wavelength components which can be absorbed by the isotope H<sup>35</sup>Cl and the other spectrum is missing those wavelength components which can be absorbed by the isotope H<sup>37</sup>Cl.

It is seen that the analyzer essentially compares the amount of H<sup>35</sup>Cl and H<sup>37</sup>Cl in the sample tube, but since there is three times as much H<sup>35</sup>Cl than H<sup>37</sup>Cl in any sample, the result is a direct measurement of the hydrogen chloride in the sample.

As shown in Figure 2.2, the output of the device is obtained from the ratio:

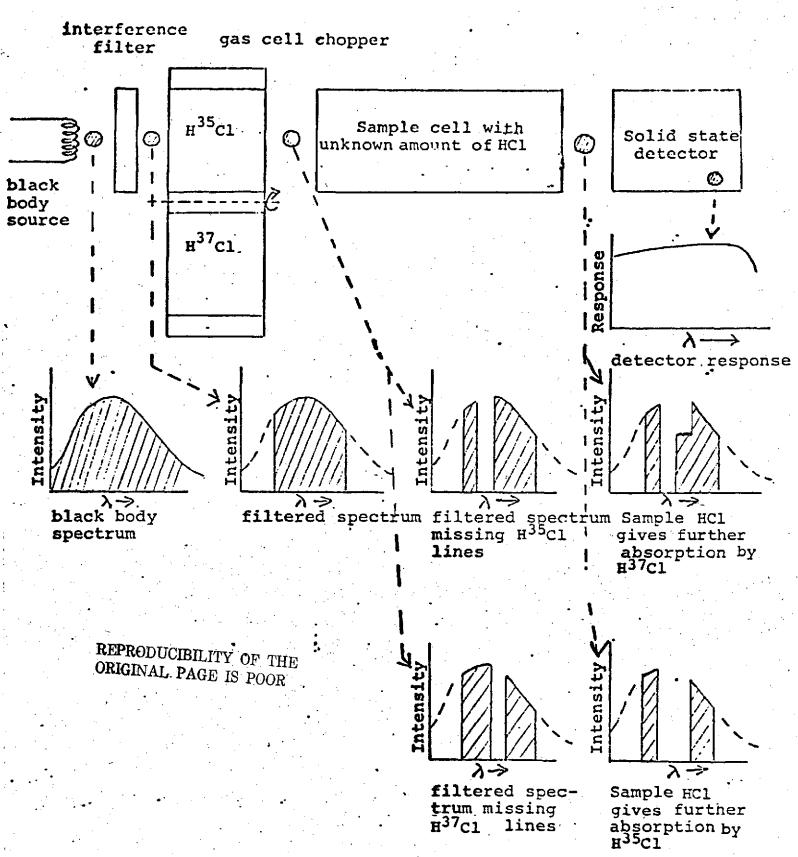


Figure 2.1 Schematic diagram illustrating the principle of the dual isotope Gas
Filter Correlation Analyzer as applied to the detection of HCl.

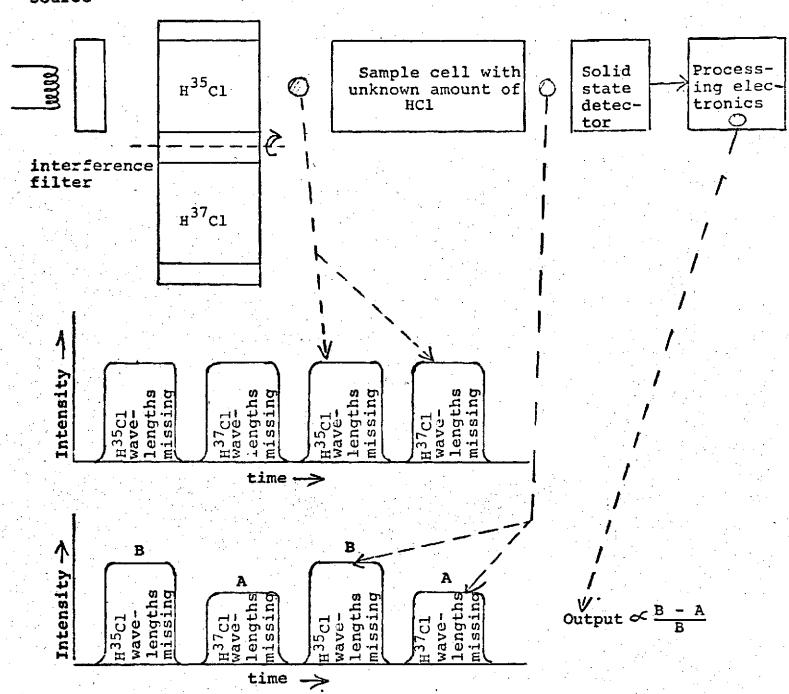


Figure 2.2. Dual Isotope Gas Filter Correlation NDIR Analyzer for HCl. H<sup>37</sup>Cl is a stable isotopic form of hydrogen chloride, H<sup>35</sup>Cl is the more common form. The chopper blade contains gas cells which chop the infrared beam into an alternating sequence of beams which are missing the H<sup>35</sup>Cl and then the H<sup>37</sup>Cl components. The beam missing the H<sup>35</sup>Cl wavelength components is only slightly further reduced by any HCl in the sample tube. The beam missing the H<sup>37</sup>Cl wavelength components is strongly reduced by HCl in the sample tube.

HCl concentration = Const. x beam rich in  $H^{37}Cl$  - beam rich in  $H^{35}Cl$  beam rich in  $H^{37}Cl$ 

or HCl concentration = Const. 
$$x \frac{H^{37}C1 - H^{35}C1}{H^{37}C1} = \frac{B - A}{B}$$
 (2.1)

Thus instrument output is independent of variation in most instrument or gas parameters. If, for example, the gas in the sample region were suddenly to become 50% obscuring because of the arrival of dense smoke, the ratio (2.1) becomes

concentration = Const. x 
$$\frac{1/2 \text{ H}^{37}\text{Cl} - 1/2 \text{ H}^{35}\text{Cl}}{1/2 \text{ H}^{37}\text{Cl}}$$
 = Const. x  $\frac{\text{H}^{37}\text{Cl} - \text{H}^{35}\text{Cl}}{\text{H}^{37}\text{Cl}} = \frac{\text{B} - \text{A}}{\text{B}}$ 

and the instrument output remains unchanged in its evaluation of HCl concentration.

The instrument is stable against variation in many other factors including source intensity drift, window dirt, most electronic drift and detector sensitivity drift.

A different and changing amount of dirt on the H<sup>35</sup>Cl and the H<sup>37</sup>Cl windows of the chopper produces first order instrument drift. These windows are, however, entirely separated from the sample gas stream and from any contact with the external environment, and differential dirt on them will not be a problem.

#### 3. DESCRIPTION OF THE PROTOTYPE HC1 ANALYZER

A schematic diagram of the gas filter correlation analyzer designed to monitor HCl is shown in Figure 3.1. The infrared source is an automotive-type cigarette lighter, encased in a ceramic housing and resistance heated to about 1000° K. Radiation from the source in the forward direction passes through two beamdefining apertures in the walls of an enclosure which surrounds the rotating chopper assembly. Two cells containing respectively mixtures of H<sup>35</sup>Cl and H<sup>37</sup>Cl in nitrogen are mounted in the chopper assembly and rotated at approximately 80 Hz so as to alternatively filter the radiation entering the sample cell. Radiation transmitted by the rotating chopper assembly is then passed through a 100 cm sample cell consisting of a glass tube 1" in diameter and gold plated on the inside to yield a high reflection coefficient. Side ports at each end of the sample tube permit gas to be flowed through the sample tube. Radiation which is transmitted by both the sample cell and interference filter is collected by a cone and reflected onto a temperature stabilized PbSe detector. The interference filter centered at 3.6µm has a half power bandwidth of 0.18µm and limits the transmitted radiation to that of the P branch of HCl. All infrared transmitting windows are sapphire.

The HCl gas filter cells are fabricated by fusing 1" diameter sapphire windows to either end of a .45" long sleeve of Corning type 7520 glass. A glass side tube connects the filter cell through a glass-to-metal seal to the gas mixing manifold while filling the cell with the required gas mixture, after which the side tube is torched off within 1/2" of the cell wall. After each cell has been filled with the appropriate mixture it is epoxied into its own aluminum holder which is in turn screwed to the rotating chopper assembly. A corrosive resistant manifold was constructed for the purpose of filling the filter cell with the required gas mixture. The pressures of gases introduced into the cell are monitored with a Baratron capacitive-type manometer. The isotopically enriched HCl was obtained from Oak Ridge National Laboratory. The H<sup>35</sup>Cl is 99.35% <sup>35</sup>Cl enriched with the balance being H<sup>37</sup>Cl, and the H<sup>37</sup>Cl is

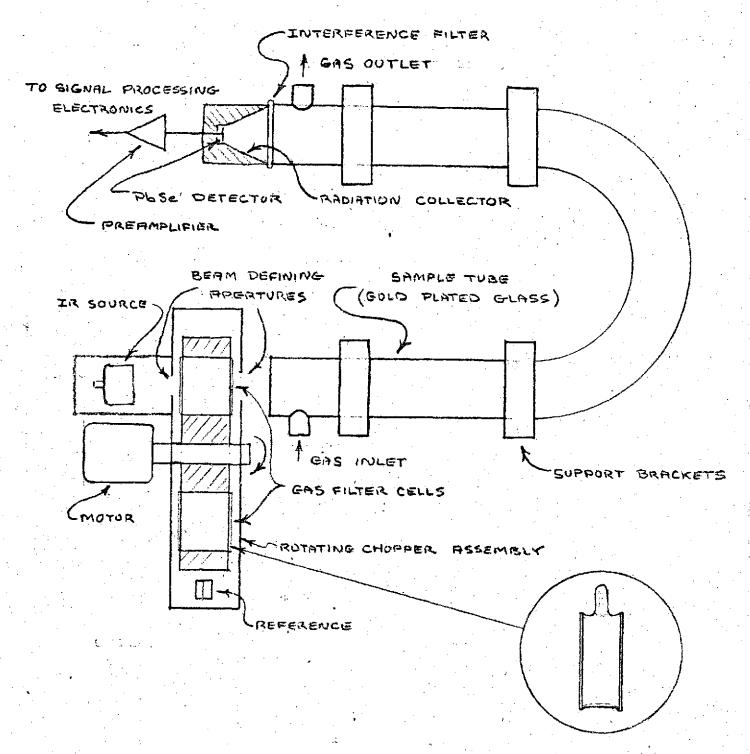


Figure 3.1. Schematic of the prototype HCl gas filter correlation analyzer. Details of the gas filter cell are shown in the inset.

90.35% enriched with the balance being H<sup>35</sup>Cl. Prior to filling, each cell was evacuated on a diffusion pump vacuum system and baked to about 150° C overnight. The procedure for filling a cell was to first introduce the required partial pressure of HCl into the gas cell and then isolate the cell. The HCl in the manifold was then retrieved by freezing the isotope supply. (The vapor pressure of HCl is 10<sup>-5</sup> Torr at liquid nitrogen temperature.) High purity nitrogen was then introduced into the cell yielding a total pressure of 760 Torr. The cell was again isolated. Finally the cell was immersed in liquid nitrogen to reduce its interior pressure to about 0.25 of an atmosphere and the cell torched off. The gas mixture contained within the cells has been found to be quite stable which is not surprising because of the fused construction.

The cell filling pressure used in a gas filter correlation analyzer may be chosen to satisfy a variety of criteria. As the cell gas filling approaches optically "thin" conditions, the sensitivity of the analyzer decreases and eventually approaches zero. For optically "thick" cells the sensitivity of the analyzer is almost constant, however the selectivity of the analyzer (i.e., its ability to reject or show no response to other gases) in general worsens as the cell optical thickness increases. Thus the choice of actual gas concentration used in chopper cells is usually a compromise between the desired sensitivity and selectivity.

Andros had in the past (with gases other than HCl) used cell fillings to yield an optical "thickness" such that  $k_{om}u=8$  ( $k_{om}$  is the maximum peak LR absorption coefficient of the gas, located at the center of the strongest absorption line; u is the optical thickness of the gas in atm cm).

For HCl  $k_{om} \approx 45 \text{ atm}^{-1} \text{ cm}^{-1}$ . The physical length of the cells used in this program was 1.15 cm and thus the filling pressure of HCl to satisfy the above rule can be calculated as follows:

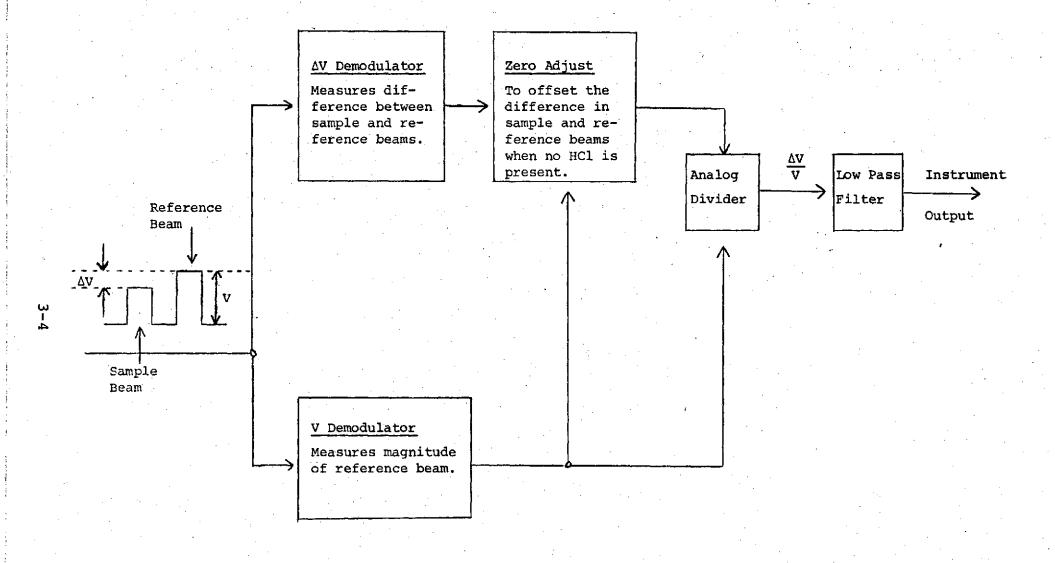


Figure 3.2. Block diagram of the Signal Processing Electronics.

 $k_{om}$  x Length x partial pressure = 8.  $45 \times 1.15 \times p = 8$ . Hence p - .155 atm = 118 Torr.

All of the subsequent results quoted in Section 4 of this report were taken with an HCl cell filled to a partial pressure of 115 Torr HCl and a total pressure of 760 Torr  $\rm N_2$  + HCl. Since the analyzer yielded sensitivity and selectivity consistent with the program goals with this cell filling, it was considered not warranted to conduct extensive experiments with alternate cell fillings. It is, however, worth mentioning that early in the program one cell was filled to an HCl partial pressure of 30 Torr, or one-fourth of the above value. When the 30 Torr cell was used in the analyzer, the sensitivity (as expected) decreased and was about two-thirds of the value found with the 115 Torr cell. The results of Section 4 are thus relatively insensitive to actual filling pressure, and the use of HCl filling pressures anywhere in the range of 50 - 200 Torr would probably have yielded closely similar analyzer performance.

The temperature of the PbSe detector is thermoelectrically stabilized using a thermistor attached to the detector substrate and servoing the cooler power to hold its resistance constant. Optical pickups are located at appropriate points around the rotating chopper assembly to provide reference signals for the synchronous detection electronics. As explained in Section 2, the infrared radiation reaching the detector during each rotation of the chopper assembly consists of two distinct beams. One of these beams will be attenuated according to the concentration of HCl in the sample gas while the other is relatively unaffected. A block diagram of the signal processing electronics is shown in Figure 3.2.

There are two demodulators in the signal processing electronics. One of these, the "V" demodulator, measures the magnitude of the reference beam. The second, "AV" demodulator, measures the difference between the sample and reference beams from which is subtracted

a fraction of the reference beam to correct the zero offset due to the natural difference in the intensities in the sample and reference beams. When there is no HCl present in the sample gas, then the zero offset is adjusted to provide zero output from the AV demodulator. The presence of HCl in the sample will now be registered as the deviation of the AV demodulator output from zero. Since a given concentration of HCl will always absorb the same fraction of the incident radiation, this fraction is derived by performing the analog division of the signals from the AV and V demodulators. The output of the analog divider is then tailored to the desired response time using a two-pole low-pass filter to yield the instrument output.

#### 4. RESULTS OBTAINED WITH THE PROTOTYPE HC1 ANALYZER

## 4.1 Test Apparatus

The analysis of a gas stream for its HCl content is often complicated by the presence of water vapor either in the sample gas or on the walls of the sample cell. In the present optical design, the simultaneous condensation of HCl and water vapor on the walls of the sample cell produces a very significant decrease in the reflection coefficient of the infrared radiation (incident at glancing angles) and hence overall optical transmission, which in turn results in an unacceptable zero instability. The following results were therefore obtained with the system thoroughly purged of either HCl or water vapor, when the other gas was being studied. The zero instability of the current prototype analyzer in the presence of both HCl and water vapor is not expected to be present using sample cell designs in which the glancing angle wall reflections of the present design are avoided. Hence the sensitivity, response time, specificity and stability inherent in the gas filter correlation analyzer approach to the detection of HCl can still be evaluated with the prototype unit developed during the current contract.

A schematic diagram of the gas mixing manifold used to obtain required HCl mixtures in  $N_2$  is shown in Figure 4.1. A gas dilution manifold consisting of two flow meters (one of which is made solely from glass for use with HCl), teflon sampling lines and fittings, and several valves, is used to produce known concentrations and flow rates of HCl in  $N_2$ . A single stage corrosive-resistant regulator is used with the HCl supply which is either pure HCl or a mixture of 150 ppm HCl in  $N_2$ .

Three sample tubes have been used to perform these studies. The main sample cell is a 100 cm long, 0.88 inch I.D. glass tube, bent in the form of a "U" with the internal surface gold-plated and the ends sealed with sapphire windows. All of the test results

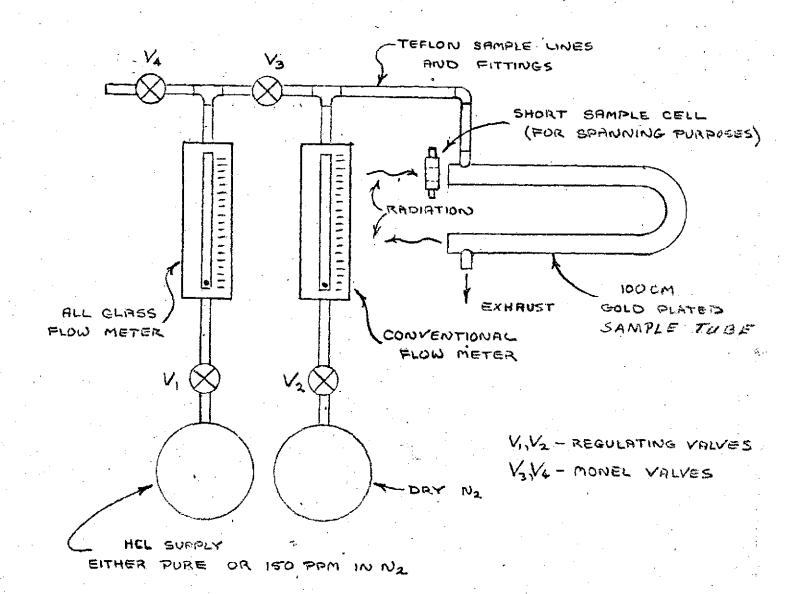


Figure 4.1. Schematic diagram of the gas mixing manifold used to obtain the required HCl mixtures in  $N_2$ . Two of the three sample cell configurations used are also shown.

quoted have been obtained with this sample cell, with the exception of the moist HCl tests described in Section 4.6, which used the relatively open cell configuration shown in Figure 4.6. A third sample cell, with an optical path length of 0.5 cm, was introduced into the optical path of the "U" tube for additional HCl calibration tests. See Figure 4.1. This cell is fabricated by mounting two sapphire windows over a 0.88 inch diameter hole in a block of teflon. Two 0.12 inch holes in the cell walls enabled gas flow through the cell.

### 4.2 Sensitivity

Two approaches were taken to spanning the instrument starting respectively with a calibration mixture of 150 ppm HCl in  $\rm N_2$ , manufactured by Precision Gas Products, and pure HCl. The calibration mixture, when used with the 100 cm sample tube, yielded an absorber thickness of 0.015 atm cms, while pure HCl was diluted with pure  $\rm N_2$  using the apparatus shown in Figure 4.1 to a level which provided a comparable absorber thickness when flowed through the short (0.5 cm) sample cell. The fraction of the transmitted radiation absorbed by the HCl in each case agreed within 10% and therefore the 150 ppm HCl mixture was used as the calibration standard for subsequent tests.

Figure 4.2 shows the response of the analyzer to 9 ppm HCl in  $N_2$  which was produced by dilution of the calibration mixture. The peak-to-peak noise equivalent level of HCl can be seen to be about 0.3 ppm for the conditions of an electronically determined 10--90--8 time response of 2.2 seconds. From these results, the rms noise equivalent concentration of HCl can be estimated to be about 0.06 ppm. This noise level could be reduced by a factor of two, if the 5 sapphire windows in the optical path (whose transmission is 87--8) were replaced by anti-reflection coated silicon windows (of 99% transmission at  $3.5\mu\text{m}$ ), since the transmitted power would then be doubled.

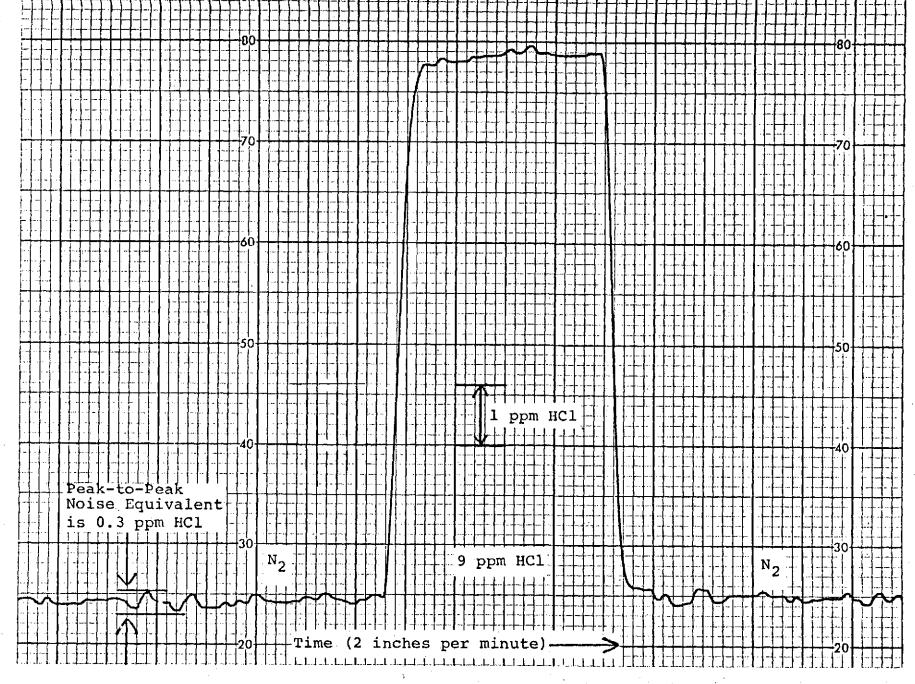


Figure 4.2. Response of the gas filter correlation analyzer to 9 ppm HCl using an electronically determined time response of 2.2 seconds for 10% to 90% change at the output. Note that the actual response time in this example has been limited by the low sample gas flow rate.

#### 4.3 Response Time

Whereas the total instrument response time shown in Figure 4.2 was limited by the gas flow rate, an example of the analyzer's response at very high flow rates (in which the response is now determined by the electronic time constant of 2.2 seconds) is shown in Figure 4.3. It should be noted that the apparent variation in response to the 9 ppm HCl was due to instabilities in the gas dilution system at the very high flow rates used.

## 4.4 Specificity

An example of the analyzer's response to 1000 ppm  $\mathrm{CH_4}$ , 320 ppm n-hexane, 8%  $\mathrm{CO_2}$  and 10%  $\mathrm{CO}$  is shown in Figure 4.4, and 3%  $\mathrm{H_2O}$  vapor in Figure 4.5. There is no measureable effect due to  $\mathrm{CO_2}$ ,  $\mathrm{CO}$  and  $\mathrm{H_2O}$  vapor while the rejection ratios for  $\mathrm{CH_4}$  and n-hexane are 2000:1 and 100:1 respectively. Shown also for comparison in Figure 4.4 is the response to 15 ppm HCl both before and after the cross sensitivity tests.

Therefore a response equivalent to 0.1 ppm HCl will not be exceeded by the above species at the levels of

| CO               | 1,000  | ppm  |
|------------------|--------|------|
| co <sub>2</sub>  | 1,000  | ppm  |
| н <sub>2</sub> о | 25,000 | ppm  |
| СН <sub>4</sub>  | 100    | ppm  |
| n-hexane         | 10     | .mag |

## 4.5 Stability

Since the analyzer maintains span stability by computing the ratio of the absorbed power to transmitted power, then the instrument span can only change if gas were to leak out of the chopper cells. Neither a change in span nor repeated measurements of the absorption spectrum of the cells using a spectrophotometer indicated any loss of gas from the cells used to obtain these results.

Instrument

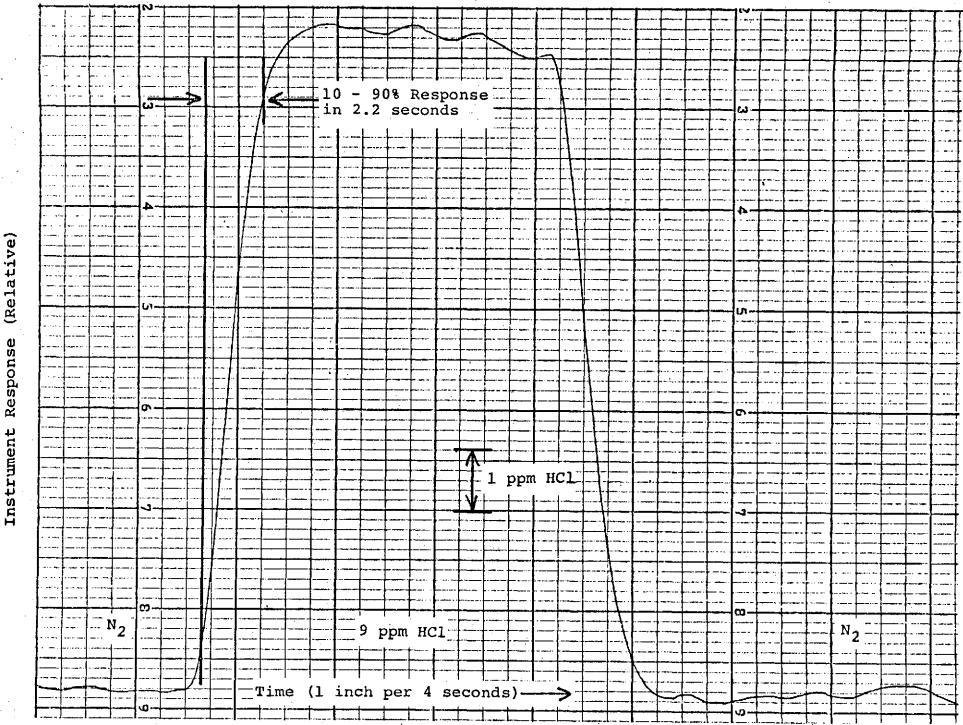


Figure 4.3. Response of the Gas Filter Correlation Analyzer to 9 ppm HCl, having a flow rate of about 1 liter per second, showing the 10-90% total systems response of 2.2 seconds. The response to 9 ppm HCl is not steady because of variations in the gas NOTE: dilution system.

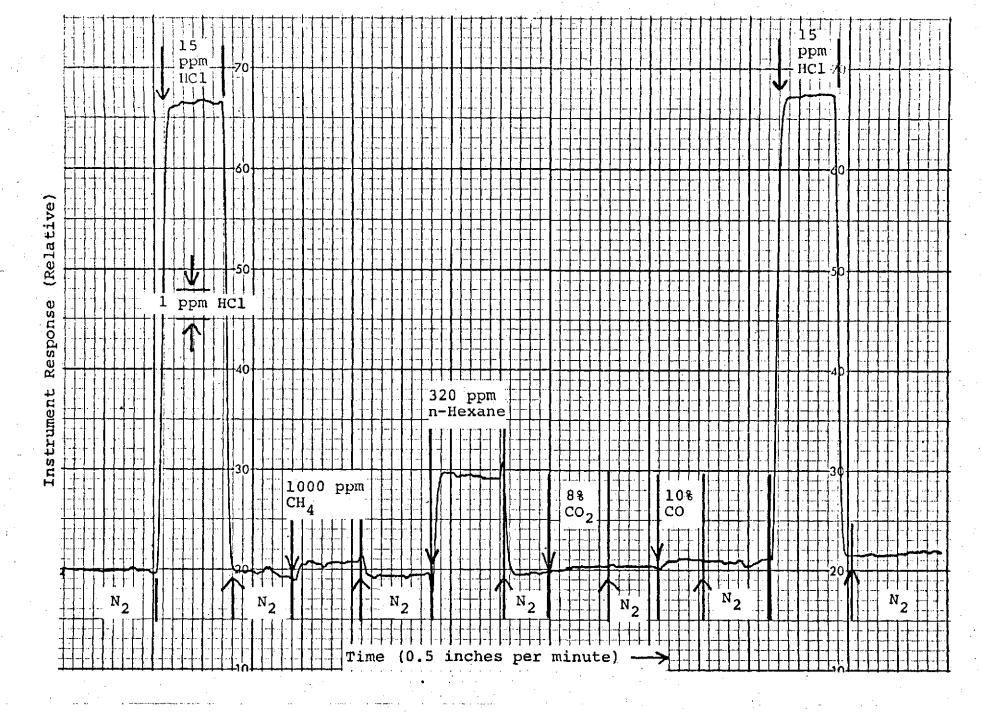


Figure 4.4. Sensitivity of the HCl gas filter correlation analyzer to relatively high levels of CH<sub>4</sub>, n-Hexane, CO<sub>2</sub>, CO and HCl in N<sub>2</sub>.

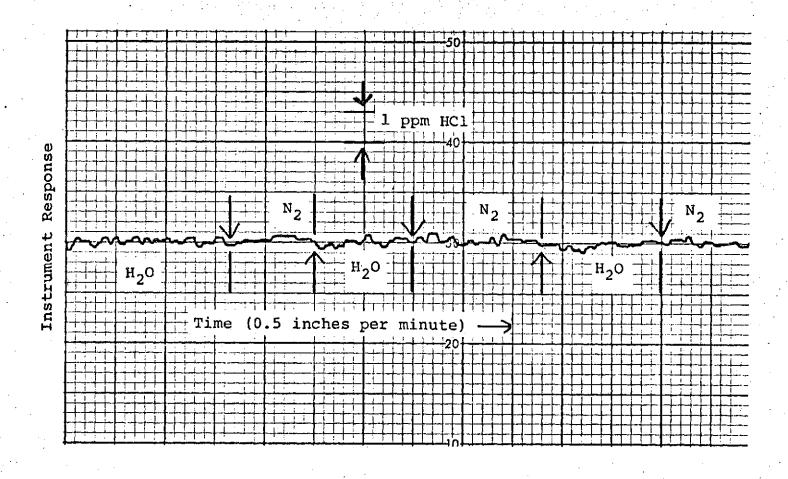


Figure 4.5 Response of the HCl gas filter correlation analyzer to alternate streams of dry  $N_2$  and a  $N_2$  stream saturated with  $H_2O$  vapor at 75° F. The instrument is temperature stabilized at 120° F.

A typical example of the zero stability obtained with the 100 cm "U" tube while flowing N<sub>2</sub> through the sample cell is shown in Figure 4.2, in which there has been a zero drift of less than 0.2 ppm over the measurement time of approximately twenty minutes. These results were obtained with the optical assembly open and sitting on a bench in the laboratory. Improved thermal insulation and/or electronic temperature correction would further improve the zero stability. Measurements performed with the prototype unit placed in an environmental chamber yielded a zero drift with temperature of 0.25 ppm HCl per °C, which can be considerably reduced by electronic temperature compensation.

Since the radiation which is transmitted through the sample cell undergoes many reflections at glancing angles, the condensation of H<sub>2</sub>O vapor on the walls of the sample tube when HCl is present produces a very significant reduction in reflection coefficient. No significant problems are expected, however, using an optical system in which the radiation is at approximately normal incidence to the reflecting surface.

This latter assumption has been partially verified using the experimental arrangement shown in Figure 4.6 in which the "U" tube of the prototype HCl analyzer has been replaced by a 10 cm diameter, 10 cm long plexiglass sample cell, and the detector assembly has been repositioned so as to respond only to radiation transmitted directly through the sample cell without being reflected from its Tests have been performed in which both relatively low levels (32 ppm) and high levels (1150 ppm) of HCl have been produced in the sample cell with the balance of gas being either dry N2 or moist air containing as much as 1% H2O vapor. Since some HCl and H<sub>2</sub>O vapor can be expected to condense on the interior side of the sapphire windows of the sample cell, it is very significant that at these normal incident angles, no significant decrease in transmission of radiation through these windows has been observed when moist air replaces N2 in the sample cell (which has been previously dried thoroughly).

## 4.6 Effect of H<sub>2</sub>O Vapor on Span Sensitivity

The possibility has been raised that the interaction of the highly polar molecules HCl and  $\rm H_2O$  might result in a slight displacement of the absorption band of the HCl in the sample cell from that in the gas correlation cells, and thereby produce a reduced sensitivity to HCl in the presence of moisture. The prototype was therefore modified to that of an essentially open-cell configuration as shown in Figure 4.6 in which there is no significant loss of either HCl or  $\rm H_2O$  from that part of the sample gas within the optical path.

Examples of the test results obtained, shown in Figures 4.7 and 4.8 for 1150 ppm and 32 ppm HCl respectively, do not show any effect of the  $\rm H_2O$  vapor.

Referring to the chart recorder data of Figure 4.7, the baseline is first established by flowing dry  $N_2$  into the sample cell. Next, pure HCl at 23 cc/min and dry N2 at 21 liters/min are simultaneously turned on, giving a mixture of approximately 1150 ppm HCl in N2 in the sample tube. Then the N2 stream is replaced by air at room humidity, giving approximately 1150 ppm HCl in humid air in the sample tube. This sequence is repeated and finally the HCl is shut off completely and the flow reverts to dry  $N_2$ . should be noted that the experimental procedure employed was to adjust the laboratory air and dry No flow rates to give identical readings on the common flow meter. Since the density of air is greater than N2, this results in the flow rate of air being 2% less than that of N2 and hence the concentration of HCl produced in air would be 2% greater than that in N2, which corresponds to just the difference in analyzer response observed on the chart recording. Furthermore, the transients observed when changing between dry N2 and laboratory air are produced by their momentary interruption resulting in a brief rise in the HCl concentration in the optical path. Within the limits set by detector noise, the

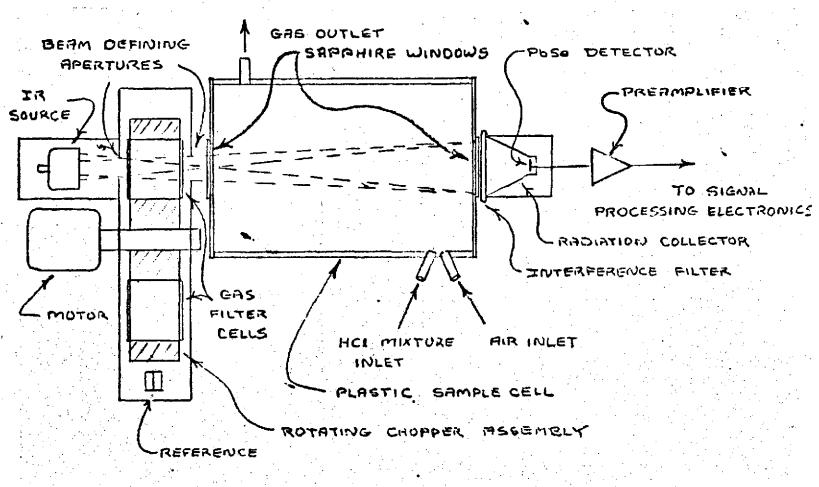


Figure 4.6. Schematic diagram of the modified prototype HCl analyzer in which the "U" tube sample cell has been replaced by a relatively large diameter plexiglass sample cell so that the possible effects (if any) of H2O vapor on the absorption spectrum of HCl can be determined.

Figure 4.7. Response of the modified gas filter correlation analyzer to HCl which is mixed in the sample cell with

- (a) Dry  $N_2$ .
- (b) Moist air. The concentration of water vapor in the sample cell is 1.0%.

#### Notes on Figure 4.7:

- 1. The transients observed when changing between dry N<sub>2</sub> and laboratory air are produced by their momentary interruption.
- 2. The experimental procedure employed was to adjust the laboratory air and dry N<sub>2</sub> flow rates to give identical readings on the common flow meter. Since the density of air is greater than N<sub>2</sub>, this results in the flow rate of air being 2% less than that of N<sub>2</sub> and hence the concentration of HCl produced in air would be 2% greater than that in N<sub>2</sub>, which corresponds to just the difference in analyzer response observed on the graph.
- 3. The conclusion drawn from this experiment is that water vapor does not desensitize the HCl Gas Filter Correlation Analyzer at the levels of gas used.

results shown in Figure 4.8 for 32 ppm HCl do not exhibit any effect due to H<sub>2</sub>O vapor. It should be noted that the apparent 10-fold decrease in analyzer sensitivity over that shown in Figure 4.2 is merely due to the reduction in sample path length by a factor of 10. While conclusive experiments to show that the HCl and moist air streams are mixing well within the sample cell are not easy, there are two pieces of supporting evidence. Firstly, a smoke stream introduced in place of the HCl appears to disperse very rapidly and uniformly; and secondly, the fraction of the transmitted radiation which is absorbed by the HCl during these tests corresponds to that predicted on the basis of the absorption law derived during the studies performed with the "U"-shaped sample tube in which dry HCl was uniformly dispersed.

Hence we conclude that water vapor does not desensitize the HCl gas filter correlation analyzer at the levels of gas used.

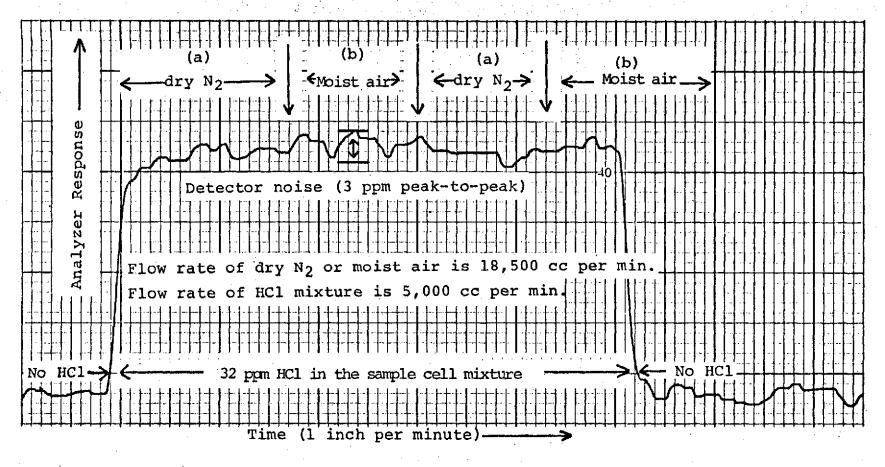


Figure 4.8. Response of the modified HCl gas filter correlation analyzer to 150 ppm HCl in N<sub>2</sub> which is mixed in the sample cell with

- (a) Dry  $N_2$ .
- (b) Moist air. The concentration of water vapor in the sample cell becomes 0.6%.

NOTE: With the limits set by detector noise, these results do not indicate any effect of water vapor on the sensitivity of the HCl gas filter correlation analyzer at relatively low levels of HCl.

#### 5. CONCLUSIONS AND RECOMMENDATIONS

The results of this program have demonstrated that the prototype HCl analyzer employing an NDIR Gas Filter Correlation technique can measure the concentration of HCl in dry gas samples with a peak-to-peak noise level of approximately 0.3 ppm and a time response (10% to 90%) of about 2 seconds, while maintaining an adequate rejection of any other gases likely to be present in the atmosphere.

The prototype analyzer used an absorption pathlength of 100 cms, and thus the peak-to-peak noise level of 0.3 ppm corresponds to an "optical" thickness of HCl gas of 3 x  $10^{-5}$  atm cm.

The response of the prototype analyzer to the gases  $\mathrm{CH_4}$ ,  $\mathrm{C_6H_{14}}$  (n-Hexane),  $\mathrm{CO_2}$  and  $\mathrm{H_2O}$  was measured. For the cases of  $\mathrm{CH_4}$  and  $\mathrm{C_6H_{14}}$ ,  $2 \times 10^{-2}$  and  $10^{-3}$  atm cm of these gases respectively showed a response equivalent to  $1 \times 10^{-5}$  atm cm of HCl. For the cases of  $\mathrm{CO_2}$  and  $\mathrm{H_2O}$  5, 4 and 3 atm cm of these gases respectively showed an immeasurably small response which was equivalent to less than  $1 \times 10^{-5}$  atm cm of HCl.

Furthermore, experiments have been performed which have demonstrated that the span stability of the HCl gas filter correlation analyzer is unaffected by the presence of water vapor. The only practical limitation encountered has been an excessive zero drift which is produced by the simultaneous condensation of H<sub>2</sub>O and HCl on the walls of the sample cell.

The recommendation is made that by incorporating a relatively open-volume, multiple path sample cell into the prototype analyzer, then not only should the required zero stability in the presence of moist HCl be achieved, but that this configuration would be appropriate for both ground station and airborne monitoring of trace quantities of HCl in the ambient atmosphere.